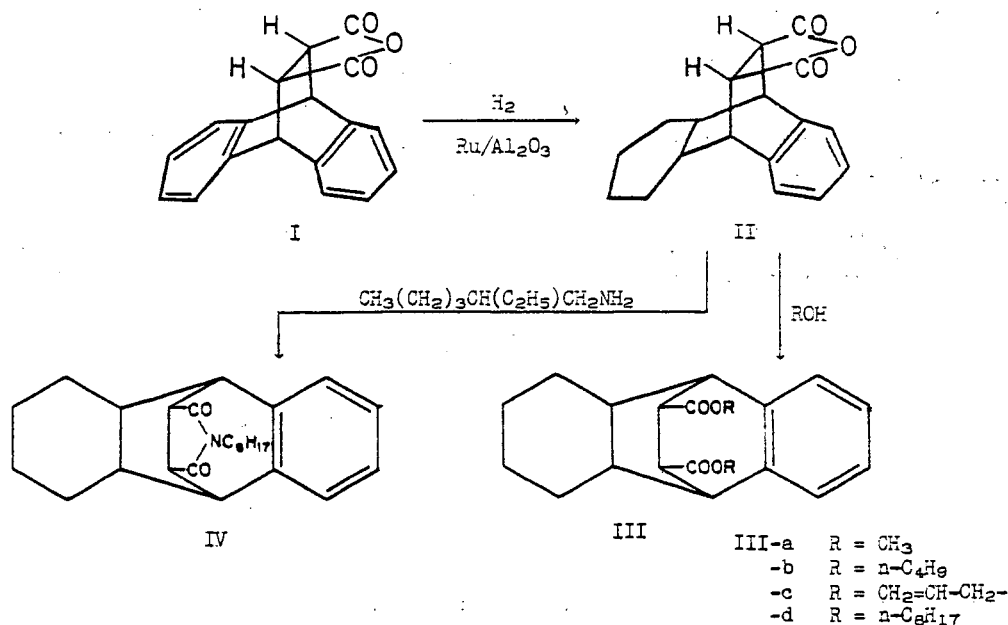


HYDROGENATION OF DIELS-ALDER ADDUCTS OF ANTHRACENE

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The Diels-Alder condensation of anthracene with dienophiles is a reversible, temperature-dependent reaction.¹ At higher temperatures, usually above 200° C, the equilibrium is shifted in favor of the polycyclic hydrocarbon.² Pyrolysis of anthracene adducts has been suggested as a means of purifying anthracene or unsaturated alcohols.³ The low thermal stability of these adducts excludes their use as potential starting materials for the preparation of polymers. It was thought that hydrogenation of one or both benzene rings in these adducts would prevent the pyrolytic reversal reaction and produce compounds of higher thermal stability. This was found to be the case when two anthracene adducts, 9,10-dihydroanthracene-9,10-endo- α,β -succinic anhydride (I)⁴ and 11-methyl-9,10-dihydro-9,10-ethanoanthracene (VIII),⁵ were hydrogenated in the presence of ruthenium catalyst. Hydrogenation of adduct I under high pressure at 145-150° C in the presence of ruthenium-on-alumina catalyst led to the absorption of three moles of hydrogen per mole of I, producing 1,2,3,4,4a,9,9a,10-octahydroanthracene-9,10- α,β -succinic anhydride (II).



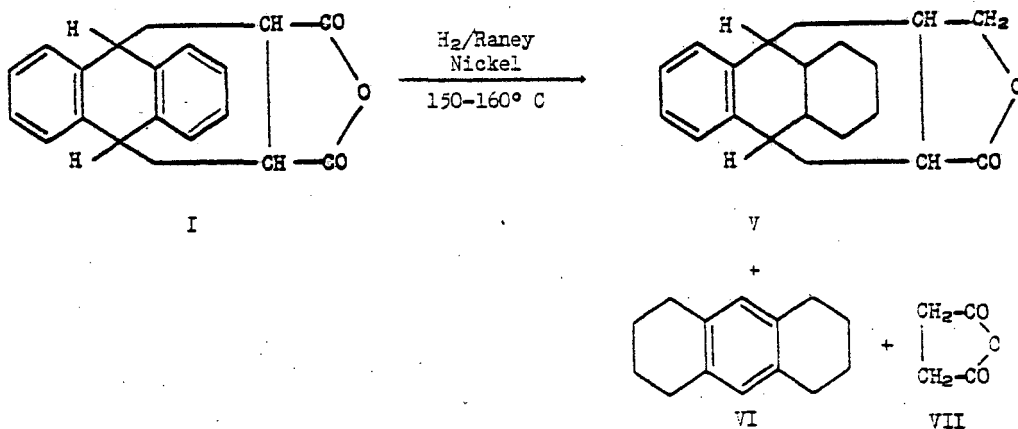
The infrared and ultraviolet spectra were consistent with structure II. The ultraviolet spectrum was that of an ortho-disubstituted benzene, and the infrared showed absorption bands characteristic of anhydride and ortho-disubstituted benzene groups.

Under the conditions employed, only one benzene ring was hydrogenated. The failure of the second benzene ring to undergo hydrogenation can be explained by steric effects as follows. The molecule of adduct I, which contains a meso-dihydroanthracene skeleton, is non-planar. It has been shown that 9,10-dihydroanthracene is bent about the line joining carbon atoms 9 and 10, each half of the molecule being planar but the two halves inclined to each other at an angle of approximately 145° .^{6,7} Assuming that addition of hydrogen to the benzene rings requires a flatwise adsorption of the unsaturated ring against the catalytic surface, it is likely that due to the bent configuration of adduct I and to the hindering effect of the bulky anhydride group, only one of the benzene rings can be hydrogenated.⁸ Inspection of the Godfrey molecular model of the adduct (I) confirms these expectations.

The hydrogenated adduct II, m.p. $145\text{--}165^\circ\text{C}$, was a mixture of stereoisomers, and no attempt was made to separate them and determine their configuration. Several derivatives of interest as potential plasticizers or pesticides, such as the diesters (III-a, b, c, d) and the N-substituted imide (IV), were prepared by standard procedures from II.

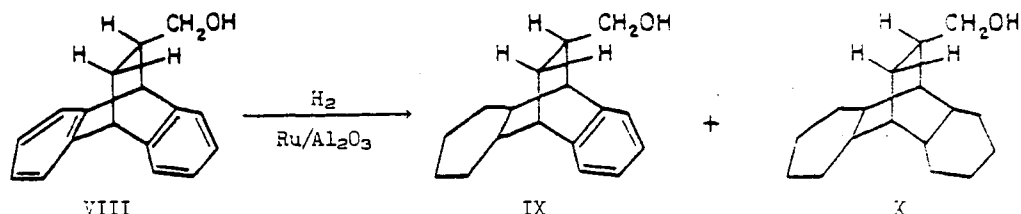
The foregoing results show that in the presence of a ruthenium catalyst, a selective hydrogenation occurred, resulting in the reduction of the aromatic ring but not affecting the succinic anhydride group of the adduct (I). In contrast, the anhydride group is attacked when a substituted succinic anhydride^{9,10} is hydrogenated in the presence of palladium or platinum catalyst, the products obtained being hydroxy-lactones, lactones, and β -methyl acids. The reduction of adduct I in the presence of Raney nickel at 160°C was also non-selective, providing a mixture of compounds. These were 1,2,3,4,4a,9,9a,10-octahydro-9,10-ethanoanthracene-11-methylol-12-carboxylic acid lactone (V), produced by an attack on the aromatic ring and the anhydride group; s-octahydroanthracene (VI); and succinic anhydride (VII).

Products VI and VII could have been formed either by hydrogenolysis or thermal decomposition of the adduct (I) followed by hydrogenation of the intermediates.



The lactone (V), m.p. $125\text{--}145^\circ\text{C}$, was a mixture of stereoisomers.

In contrast to I, the hydrogenation of 11-methylol-9,10-dihydro-9,10-ethanoanthracene (VIII) in the presence of ruthenium catalyst proceeds further with some reduction of both aromatic rings, affording a mixture of 11-methylol-9,10-ethano-1,2,3,4,4a,9,9a,10-octahydroanthracene (IX) and 11-methylol-9,10-ethanoperhydroanthracene (X) in a variable ratio depending upon the reaction time.



Hydrogenation of both aromatic rings of VIII occurred, since the hindering effect of the hydroxymethyl group is smaller than that of the rigid and bulky anhydride group of I. As in the previous case, no attempt was made to separate the stereoisomers.

Experimental

1,2,3,4,4a,9,9a,10-Octahydroanthracene-9,10- α , β -succinic Anhydride (II)

A mixture of 83 g. of 9,10-dihydroanthracene-9,10-endo- α , β -succinic anhydride (I) (m.p. 261-262° C), 250 ml. of dioxane, and 6.0 g. of 5% ruthenium-on-alumina catalyst was placed in an "Aminco" autoclave, and hydrogen was admitted up to 1350 p.s.i. The vessel was shaken and heated for 16 hours at 145-148° C, after which the absorption of hydrogen ceased. The amount of hydrogen absorbed corresponded to about 3 moles of hydrogen per mole of I. After cooling, the catalyst was removed by filtration and washed with acetone. The filtrate and the washing were combined, and the solvents were removed by distillation, first at atmospheric pressure, then under vacuum. The solid residue, after washing with petroleum ether (30-60° C), gave 71 g. (84%) of 1,2,3,4,4a,9,9a,10-octahydroanthracene-9,10- α , β -succinic anhydride (II), m.p. 145-165° C. A sample of the anhydride, crystallized from ethyl acetate-petroleum ether, melted at 175-177° C. Infrared absorption maxima: 5.45, 5.70, and 13.0 μ . Ultraviolet absorption spectrum in methylene chloride: λ_{max} 247 m μ (ϵ 248), 253 (270), 260 (297), 263 (216), and 267 (230).

Anal. Calcd. for $\text{C}_{18}\text{H}_{18}\text{O}_3$: C, 76.57; H, 6.43; Molecular Weight, 282.3.
Found: C, 76.67; H, 6.57; Molecular Weight (Alkaline Titration), 283.3.

In order to determine its heat stability, II was heated for 6 hours in air to 230-240° C. A slight discoloration, but no degradation, occurred.

In a second experiment, a modified procedure was employed for purifying the crude hydrogenation product. After separation from the catalyst and removal of the solvent, the solid residue was heated with 5% sodium hydroxide for 5 minutes on a steam bath. After cooling and washing with ether to remove the non-acidic products, the aqueous layer was acidified with 15% hydrochloric acid. The precipitated solid, after washing with water and drying, gave the adduct (II) in a yield of 85%.

Dimethyl 1,2,3,4,4a,9,9a,10-Octahydroanthracene-9,10- α , β -succinate (III-a)

Seventeen grams of 1,2,3,4,4a,9,9a,10-octahydroanthracene-9,10- α , β -succinic anhydride (II) and 200 ml. of methyl alcohol saturated at 5° C with anhydrous hydrogen

chloride were heated under reflux for 6 hours. After cooling, the precipitated diester was filtered, washed with water, and dried to yield 15.2 g. (77%) of III-a, m.p. 122-145° C, which crystallized from hexane-ethyl acetate (10:1), m.p. 145-147° C.

Anal. Calcd. for $C_{20}H_{24}O_4$: C, 73.14; H, 7.37.
Found: C, 73.49; H, 7.53.

Dibutyl 1,2,3,4,4a,9,9a,10-Octahydroanthracene-9,10- α,β -succinate (III-b)

A mixture of 1,2,3,4,4a,9,9a,10-octahydroanthracene-9,10- α,β -succinic anhydride (17 g.) and n-butyl alcohol saturated with anhydrous hydrogen chloride (50 ml.) at 5° C in benzene (50 ml.) was heated under reflux for 5 hours. The cooled solution was diluted with ether and washed with 5% sodium hydroxide, then with water. After removal of the solvents, the residue was distilled to yield 21 g. (85%) of the dibutyl ester, b.p. 220-225° C (1.5 mm.), n_D^{25} 1.5710.

Anal. Calcd. for $C_{28}H_{36}O_4$: C, 75.69; H, 8.30.
Found: C, 75.13; H, 8.62.

The procedure for the preparation of other diesters was as follows: A mixture of 1,2,3,4,4a,9,9a,10-octahydroanthracene-9,10- α,β -succinic anhydride (0.1 m.), alcohol (0.4 m.), toluene (75 ml.), and p-toluenesulfonic acid (0.5 g.) was heated at reflux until the theoretical amount of the water was collected in the trap. The cooled solution was washed with 5% sodium hydroxide, then with water, and, after removal of the solvent, the residue was distilled.

Diallyl 1,2,3,4,4a,9,9a,10-Octahydroanthracene-9,10- α,β -succinate (III-c)

b.p. 201-203° C (0.5 mm.), n_D^{25} 1.5420, 72% yield.

Anal. Calcd. for $C_{24}H_{28}O_4$: C, 75.76; H, 7.42.
Found: C, 75.86; H, 7.62.

Di-(n-octyl)-1,2,3,4,4a,9,9a,10-Octahydroanthracene-9,10- α,β -succinate (III-d)

b.p. 245-248° C (0.4 mm.), n_D^{25} 1.5025, 88% yield.

Anal. Calcd. for $C_{34}H_{52}O_4$: C, 77.82; H, 9.99.
Found: C, 77.67; H, 10.01.

N-(2-Ethylhexyl)-1,2,3,4,4a,9,9a,10-Octahydroanthracene-9,10- α,β -succinimide (IV)

To 28.2 g. (0.1 m.) of II was added 13.5 g. (0.105 m.) of 2-ethylhexylamine, and the reaction mixture was heated with stirring to 100° C and then set aside for 2 hours. It was then heated at 160-170° C for an additional 2 hours. After removal of water by distillation, the residue was vacuum distilled to give 29.9 g. (76%) of the imide (IV), b.p. 190-232° C (0.6 mm.). On cooling, the distillate crystallized to give a product melting at 58-66° C. A sample recrystallized from petroleum ether (30-60° C) melted at 72-74° C.

Anal. Calcd. for $C_{26}H_{35}NO_2$: C, 79.34; H, 8.96; N, 3.56.
Found: C, 79.36; H, 9.08; N, 3.30.

Hydrogenation of 9,10-Dihydroanthracene-9,10- α,β -succinic Anhydride in the Presence of Raney Nickel

An "Aminco" bomb was charged with 27.6 g. of the title adduct (I), 250 ml. of ethyl alcohol, and 10 ml. of Raney nickel catalyst, and hydrogen was admitted

under 1330 p.s.i. at 25° C. The bomb was shaken and heated at 160° C for 20 hours. The amount of hydrogen absorbed corresponded to about 13.5 moles of hydrogen per mole of the starting adduct. After cooling, the solution of the hydrogenated product was separated from the catalyst by filtration, and the catalyst was washed with ether. The filtrates were combined and the solvents removed, first at atmospheric pressure, then under vacuum. The residue, composed of an oil and a solid, was treated with ethyl alcohol. The solid, insoluble in alcohol, was separated by filtration to give 4.8 g. of s-octahydroanthracene. The filtrate, after removal of the solvent by distillation, gave 20 g. of an oil.

In order to separate acidic products from non-acidic, the oil (16 g.) was heated on a steam bath with 120 ml. of 10% sodium hydroxide solution for 2 hours, and, after cooling, ether was extracted. The non-acidic product, after elimination of ether, gave an additional 5.6 g. of s-octahydroanthracene. The total of s-octahydroanthracene isolated from the reaction mixture amounted to 10.4 g., or 56%. The alkaline solution was acidified with concentrated HCl, and the precipitated solid was separated by filtration. The aqueous filtrate, after ether extraction and removal of the solvent, afforded 0.4 g. of succinic acid. The precipitated solid (6.0 g.) was crystallized several times from ethyl acetate to yield 1,2,3,4,4a,9,9a,10-octahydro-9,10-ethanoanthracene-11-methylol-12-carboxylic acid lactone, m.p. 125-145° C. Infrared absorption maxima: 5.7 (lactone) and 13.0 μ (ortho-disubstituted benzene ring).

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51.

Found: C, 79.74; H, 7.67.

Hydrogenation of 11-Methylol-9,10-dihydro-9,10-ethanoanthracene (VIII)

A mixture of 54 g. (0.228 m.) of 11-methylol-9,10-dihydro-9,10-ethanoanthracene (m.p. 105-108° C) (VIII),¹¹ 250 ml. of ethyl alcohol, and 4.0 g. of 5% ruthenium-on-alumina catalyst was placed in an autoclave, and hydrogen was admitted up to 1630 p.s.i. The vessel was shaken and heated for 6 hours at 150° C, after which the absorption of hydrogen ceased. The amount of hydrogen absorbed corresponded to about 3.8 moles of hydrogen per mole of adduct. After removal of the catalyst and solvent, the residue was distilled to yield 46 g. (84%) of a colorless oil, b.p. 150-175° C (0.6 mm.), n_D^{25} 1.5480, consisting of a mixture of 11-methylol-9,10-ethano-1,2,3,4,4a,9,9a,10-octahydroanthracene and 11-methylol-9,10-ethanoperhydroanthracene in an approximate ratio of 3 to 1.

Anal. Calcd. for $3(C_{17}H_{22}O) + C_{17}H_{28}O$: C, 83.89; H, 9.70; Molecular Weight, 244.

Found: C, 83.87; H, 10.20; Molecular Weight, 248.

(From determination of the hydroxyl content by acetylation method.)

Upon cooling, the oil partially solidified. The separated solid, 11-methylol-9,10-ethanoperhydroanthracene, crystallized from hexane, melted at 102-104° C. The infrared and ultraviolet spectra of the solid product showed complete disappearance of the aromatic ring.

Anal. Calcd. for $C_{17}H_{28}O$: C, 82.80; H, 11.36.

Found: C, 82.71; H, 11.59.

A thermal stability test of the hydrogenated adducts IX and IX + X was conducted as follows: Samples of the products were heated separately in air for 4 hours at 235-240° C. The products became colored, and according to infrared spectra, partial oxidation to the aldehydes occurred (infrared, 5.85 μ). However, no change in the carbon skeleton of the products was observed.

In a similar hydrogenation run, the crude product was separated from the catalyst, a fresh portion of the catalyst (4.0 g.) was added, and the mixture was

hydrogenated further at 160° C for an additional 17 hours. The reaction mixture contained approximately 30% of IX and 70% of X.

Acknowledgement

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